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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: LIGHT-COLORED POLYCARBONATE COMPOSITIONS AND METHODS

(57) Abstract: A composition containing a bulk polycarbonate-containing resin component; a polycarbonate-siloxane copolymer in an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and a colorant composition comprising titanium dioxide having an organic coating, for example a coating comprising a polysiloxane, in which the amount of titanium dioxide is from 1 to 2.5 %, preferably 1 to 2.0% and more preferably 1 to 1.5% by weight of the total composition has both light color and good flame-retardance. The composition can be used to prepare shaped article s, particularly those with thin wall region that achieve a V0 UL fire rating at the first thickness.



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LIGHT-COLORED POLYCARBONATE COMPOSITIONS AND METHODS

Background of Invention

This application relates to polycarbonate compositions, and particularly to polycarbonate/styrenic molding compositions which are colored using titanium dioxide to produce a white or other light colored product.

Typically, blends of polycarbonate resins and styrenics include rubber particles such as polybutadiene to serve as impact modifiers. However, the addition of grafted rubbers to polycarbonate/styrenic blends results in a reduction in the flame retardancy of the blend, making it necessary to add flame-retardants that may have a detrimental effect on the high heat characteristics of the material.

Summary of Invention

The present invention provides a composition comprising:

- (a) a bulk resin component comprising a polycarbonate;
- (b) a polycarbonate-siloxane copolymer in an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and
- (c) a colorant composition comprising titanium dioxide having an organic coating, for example a coating comprising a polysiloxane, wherein the amount of titanium dioxide is from 1 to 2.5 %, preferably 1 to 2.0% and more preferably 1 to 1.5% by weight of the total composition.

The invention further provides shaped articles, having a wall thickness greater than a first thickness that are formed from a molding composition comprising:

- (a) a bulk resin component comprising a polycarbonate;
- (b) a polycarbonate-siloxane copolymer; and
- (c) a colorant composition comprising titanium dioxide.

The titanium dioxide has an organic coating, and the amount of polycarbonate-siloxane copolymer is selected such that molding composition achieves a V0 UL fire rating at the first thickness.

The invention further provides a method for forming a light colored, flame retardant polycarbonate article comprising the steps of forming a blend comprising:

- (a) a bulk resin component comprising a polycarbonate;
- (b) a polycarbonate-siloxane copolymer in an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and
- (c) a colorant composition comprising titanium dioxide having an organic coating, for example a coating comprising a polysiloxane, wherein the amount of titanium dioxide is from 1 to 2.0 %, preferably 1 to 1.5% by weight of the total composition; and forming an article from the blend.

The invention further provides a method for enhancing the flame retardance of a light colored composition comprising a bulk resin component comprising a polycarbonate; a polycarbonate-siloxane copolymer; and a colorant composition comprising titanium dioxide, said method comprising the steps of

- (a) including the polycarbonate-siloxane copolymer in the composition in an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and
- (b) selecting as the titanium dioxide a titanium dioxide having an organic coating, for example a coating comprising a polysiloxane.

Brief Description of Drawings

Fig. 1 shows the relationship of p(FTP) to %TiO₂ at various levels of polycarbonate-siloxane copolymer.

Detailed Description

Numerical values in the specification and claims of this application, particularly as they relate to polymer compositions, reflect average values for a composition that may contain individual polymers of different characteristics. Furthermore, the numerical values should be understood to include numerical values which are the same when reduced to the same number of significant figures and numerical values which differ from the stated value by less than the experimental error of the measurement technique used in the present application to determine the value.

As noted above, the addition of styrenic impact modifiers to the polycarbonates has a known detrimental effect on the flame retardancy of the composition. This problem can be overcome by the addition of polycarbonate-siloxane copolymers. However, the inventors have observed addition of titanium dioxide to polycarbonate/polycarbonate-siloxane copolymer blends to achieve light-colored products results in a reduction in the fire retardance properties of the composition. The present invention provides light colored compositions that avoid this reduction in product quality, even in the presence of rubbery impact modifiers, and thus provides useful, fire-resistant lightly colored materials which can be used in a variety of applications including computer and business machine housings, battery chargers for the telecommunications industry and electrical applications.

In a first embodiment, the invention provides a titanium dioxide-containing polycarbonate blend comprising a bulk polycarbonate resin, a polycarbonate-siloxane copolymer and a organic-coated titanium dioxide. In other embodiments, the compositions of the invention also comprise a rubber impact modifier and/or an effective flame-retarding amount of a flame retardant.

As used in the specification and claims of this application, the term "lightly-colored" refers to any coloration of the polymer blend that includes titanium dioxide as a component of the colorant composition utilized. In particular, the term lightly colored encompasses white, cream, tan and gray colorations achieved by combining

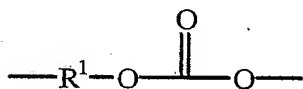
titanium dioxide with other fillers or pigments of various colors, as well as colorations achieved by mixing titanium dioxide with soluble dyes.

As used in the specification and claims of this application, the term "bulk polycarbonate resin" refers to a polycarbonate resin used as a base component of a composition. There are numerous polycarbonate resin formulations known, and the bulk polycarbonate resin portion of a given composition is selected to achieve the properties desired for a given application. Thus, the bulk polycarbonate may be a high heat polycarbonate, a polycarbonate selected to have good flow properties consistent with use in molding applications or extrusion. In general, the bulk component will be at least 50% of a total composition. In some embodiments, the bulk component is greater than 75% of the total composition.

The bulk component includes a polycarbonate resin, which may be of a single type or mixtures of two or more polycarbonate homopolymers and/or copolymers. The polycarbonate(s) may be made by either an interfacial process or a melt transesterification process. In the most common embodiment of the interfacial process, bisphenol A (BPA) and phosgene are reacted to form polycarbonate. When a melt transesterification process is used, polycarbonate is made by reacting a diaryl carbonate and a dihydric phenol. The techniques for performing melt transesterification reactions are well known, and are, for example, described in Organic Polymer Chemistry by K. J. Saunders, 1973, Chapman and Hall Ltd., as well as in a number of U.S. patents, including U.S. Pat. Nos. 3,442,854; 5,026,817; 5,097,002; 5,142,018; 5,151,491; and 5,340,905. As is known in the art, there are numerous diaryl carbonates and dihydric phenols which may be employed. The specific diaryl carbonate and the specific dihydric phenol selected will depend on the nature of the desired polycarbonate. Common diaryl carbonates which may be employed include but are not limited to diphenyl carbonate, ditolyl carbonate, bis(chlorophenyl) carbonate; m-cresyl carbonate; dinaphthyl carbonate; bis(diphenyl) carbonate; diethyl carbonate; dimethyl carbonate; dibutyl carbonate; and dicyclohexyl carbonate. Common dihydric phenols include but are not limited to bis(hydroxyaryl) alkanes such as bis(4-hydroxyphenyl)methane; 1,1-bis(4-hydroxyphenyl)ethane; 2,2-bis(4-hydroxyphenyl)propane (also known as bisphenol A); 2,2-bis(4-

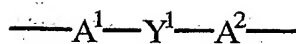
hydroxyphenyl)butane; 2,2-bis(4-hydroxyphenyl)octane; bis(4-hydroxyphenyl)phenylmethane; 2,2-bis(4-hydroxy-1-methylphenyl)propane; 1,1-bis(4-hydroxy-t-butylphenyl)propane; and 2,2-bis(4-hydroxy-3-bromophenyl)propane; bis(hydroxyaryl)cycloalkanes such as 1,1-(4-hydroxyphenyl)cyclopentane and 1,1-bis(4-hydroxyphenyl)cyclohexane; dihydroxyaryl ethers such as 4,4'-dihydroxydiphenyl ether and 4,4'-dihydroxy-3,3'-dimethyldiphenyl ether; dihydroxydiaryl sulfides such as 4,4'-dihydroxydiphenyl sulfide and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfide; dihydroxydiaryl sulfoxides such as 4,4'-dihydroxydiphenyl sulfoxide and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfoxide; and dihydroxydiaryl sulfones such as 4,4'-dihydroxydiphenyl sulfone and 4,4'-dihydroxy-3,3'-dimethyldiphenyl sulfone. In one common form of polycarbonate, the aromatic dihydroxy compound is bisphenol A (BPA) and the diaryl carbonate is diphenyl carbonate.

The polycarbonate resins used in the invention comprise repeating structural units of the formula (I):



(I)

in which at least about 60 percent of the total number of R¹ groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Preferably, R¹ is an aromatic organic radical and, more preferably, a radical of the formula (II):



(II)

wherein each of A^1 and A^2 is a monocyclic divalent aryl radical and Y^1 is a bridging radical having one or two atoms which separate A^1 from A^2 . In an exemplary embodiment, one atom separates A^1 from A^2 . Illustrative non-limiting examples of radicals of this type are -O-, -S-, -S(O)-, -S(O)₂-, -C(O)-, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene. The bridging radical Y^1 can be a hydrocarbon group or a saturated hydrocarbon group such as methylene, cyclohexylidene or isopropylidene.

Preferred polycarbonates are based on bisphenol A, in which each of A^1 and A^2 is p-phenylene and Y^1 is isopropylidene. Preferably, the average molecular weight of the polycarbonate is in the ranges from about 5,000 to about 100,000, more preferably in the range from about 10,000 to about 65,000, and most preferably in the range from about 15,000 to about 35,000. When present, the polycarbonate resin is employed in amounts of about 1 to about 99 weight percent, based on the total weight of the composition. Preferably the polycarbonate resin is present in an amount of about 1 to about 95, more preferably about 5 to about 90 and most preferably about 5 to about 85, based on the total weight of the composition.

In addition to linear homo-polycarbonates, the bulk polycarbonate resin component may include hetero-polycarbonate species including two or more different dihydric phenols or a copolymer of a dihydric phenol with a glycol or with a hydroxy- or acid-terminated polyester or with a dibasic acid or hydroxy acid. Polyarylates and polyester-carbonate resins or their blends can also be employed. Branched

polycarbonates are also useful, as well as blends of linear polycarbonate and a branched polycarbonate. The branched polycarbonates may be prepared by adding a branching agent during polymerization. These branching agents are well known and may comprise polyfunctional organic compounds containing at least three functional groups which may be hydroxyl, carboxyl, carboxylic anhydride, haloformyl and mixtures thereof. Specific examples include trimellitic acid, trimellitic anhydride, trimellitic trichloride, tris-p-hydroxy phenyl ethane, isatin-bis-phenol, tris-phenol TC (1,3,5-tris((p-hydroxyphenyl)-isopropyl)benzene), tris-phenol PA (4(4(1,1-bis(p-hydroxyphenyl)-ethyl) alpha,alpha-dimethyl benzyl)phenol), 4-chloroformyl phthalic anhydride, trimesic acid and benzophenone tetracarboxylic acid. The branching agents may be added at a level of about 0.05-2.0 weight percent. Branching agents and procedures for making branched polycarbonates are described in U.S. Patent. Nos. 3,635,895 and 4,001,184 which are incorporated by reference. All types of polycarbonate end groups are contemplated as being useful in the polycarbonate composition.

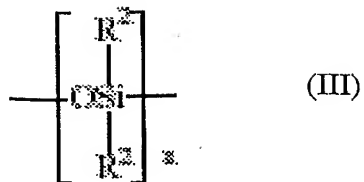
The bulk polycarbonate resin may also comprise blends of polycarbonate(s) with other non-polycarbonate thermoplastics. Non-limiting examples of thermoplastic resins that may be included in the bulk component include (a) polymers including as structural components aromatic vinyl monomers, (b) polymers including as structural components aromatic vinyl monomers and a vinyl cyanide monomers; (c) polymers including as structural component an aromatic vinyl monomers, a vinyl cyanide monomers and a rubber like polymer; (d) aromatic polyesters, (e) polyphenylene ethers, (f) polyether imides and (g) polyphenylene sulfides. Specific examples of such additional thermoplastic resins are styrene acrylonitrile copolymers and polymethyl(methacrylate).

Siloxane-polycarbonate block copolymers have been recognized for their low temperature ductility and flame retardancy and may also be utilized as the matrix for incorporating the phosphorescent pigments. These block copolymers can be made by introducing phosgene under interfacial reaction conditions into a mixture of a dihydric phenol, such as BPA, and a hydroxyaryl-terminated polydiorganosiloxane. The polymerization of the reactants can be facilitated by use of a tertiary amine catalyst.

Polycarbonate-siloxane copolymers useful in the composition of the invention are known, for example from US Patents Nos. 4,746,701, 4,994,532, 5,455,310 and 6,252,013, which are incorporated herein by reference, and are sold commercially under the name LEXAN ST by General Electric Company. Mitsubishi Engineering Plastics has described a polycarbonate type resin composition that comprises (A) 100 parts weight (pts. wt.) polycarbonate type resin which consists of (a) 1-99 wt.% of polycarbonate resin, and (b) 99-1 wt. % polycarbonate-organopolysiloxane copolymer; (B) 0.1-5 pts. wt. of phosphate type compound; and (C) 0.2-2 pts. wt. of fibril-forming polytetrafluoroethylene in JP 10007897. The polycarbonate-polysiloxane copolymer from this disclosure may also be used in the present invention.

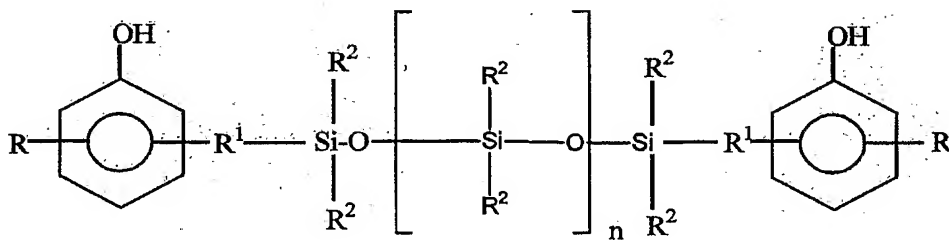
In general, the polycarbonate-siloxane copolymers useful in the invention are formed from polycarbonate blocks and poly(diorganosiloxane) blocks. The polycarbonate blocks comprise repeating structural units of the formula (I) in which at least about 60 percent of the total number of R1 groups are aromatic organic radicals and the balance thereof are aliphatic, alicyclic, or aromatic radicals. Preferably, R1 is an aromatic organic radical and, more preferably, a radical of the formula (II) wherein each of A1 and A2 is a monocyclic divalent aryl radical and Y1 is a bridging radical having one or two atoms which separate A1 from A2. In an exemplary embodiment, one atom separates A1 from A2. Illustrative non-limiting examples of radicals of this type are -O-, -S-, -S(O)-, -S(O)2-, -C(O)-, methylene, cyclohexyl-methylene, 2-[2.2.1]-bicycloheptylidene, ethylidene, isopropylidene, neopentylidene, cyclohexylidene, cyclopentadecylidene, cyclododecylidene, and adamantylidene. The bridging radical Y1 can be a hydrocarbon group or a saturated hydrocarbon group such as methylene, cyclohexylidene or isopropylidene.

The poly(diorganosiloxane) blocks comprise repeating structural units of the formula (III)



wherein each occurrence of R² may be the same or different and is selected from C(1-13) monovalent organic radicals, and n is an integer greater than or equal to 1, preferably greater than or equal to about 10, more preferably greater than or equal to about 25 and most preferably greater than or equal to about 40. It is desirable to have n be an integer less than or equal to about 1000, preferably less than or equal to about 100, more preferably less than or equal to about 75 and most preferably less than or equal to about 60. As is readily understood by one of ordinary skill in the art, n represents an average value.

In a preferred embodiment, the poly(diorganosiloxane) blocks comprise repeating structural units of the formula (IV):



(IV)

where each R may be the same or different and is selected from the group of radicals consisting of hydrogen, halogen, C(1-8) alkoxy, C(1-8) alkyl and C(6-13) aryl, R¹ is a

C(2-8) divalent aliphatic radical, R₂ is selected from the same or different C(1-13) monovalent organic radicals, and n is an integer greater than or equal to 1, preferably greater than or equal to about 10, more preferably greater than or equal to about 25 and most preferably greater than or equal to about 40. It is also preferred to have n be an integer less than or equal to 1000, preferably less than or equal to 100, more preferably less than or equal to about 75 and most preferably less than or equal to about 60. In one embodiment n is less than or equal to 50. Particularly preferred hydroxyaryl-terminated polydiorganosiloxanes are those where R₂ is methyl and R is hydrogen or methoxy and located in the ortho position to the phenolic substituent and where R₁ is propyl and located ortho or para to the phenolic substituent.

Some of the radicals included within R in the above formula are halogen radicals, such as bromo, and chloro; alkyl radicals such as methyl, ethyl, and propyl; alkoxy radicals such as methoxy, ethoxy, and propoxy; aryl radicals such as phenyl, chlorophenyl, and tolyl. Radicals included within R₃ are, for example, dimethylene, trimethylene and tetramethylene. Radicals included within R₄ are, for example, C(1-8) alkyl radicals, haloalkyl radicals such as trifluoropropyl and cyanoalkyl radicals; aryl radicals such as phenyl, chlorophenyl and tolyl. R₄ is preferably methyl, or a mixture of methyl and trifluoropropyl, or a mixture of methyl and phenyl.

The siloxane-polycarbonate block copolymers have a weight-average molecular weight (M_w, measured, for example, by Gel Permeation Chromatography, ultracentrifugation, or light scattering) of greater than or equal to about 10,000, preferably greater than or equal to about 20,000. Also preferred is a weight average molecular weight of less than or equal to about 200,000, preferably less than or equal to about 100,000. It is generally desirable to have the polyorganosiloxane units contribute about 0.5 to about 80 wt% of the total weight of the siloxane-polycarbonate copolymer. The chain length of the siloxane blocks corresponds to about 10 to about 100 chemically bound organosiloxane units. They can be prepared such as described in for example US-A-5,530,083, incorporated herein by reference in its entirety.

In the examples below, the polycarbonate-siloxane copolymer is LEXAN ST (General Electric) which is a polycarbonate/polydimethylsiloxane (PC/PDMS) copolymer

having 20% weight percent siloxane content based on the total weight of the copolymer and a block length of 50 units of the poly(diorganosiloxane) (n in formulas III and IV) The compositions in accordance with the present invention as set forth in the examples contain polycarbonate-siloxane copolymer in an amount of 18 weight percent or greater, for example 18 to 40 weight percent of the total composition, preferably 18 to 30 weight percent, and most preferably 18 to 25 weight percent. In these examples, however, the specific polycarbonate-siloxane copolymer employed contained 20% by weight of siloxane. Since it is believed to be the siloxane portion of the copolymer that is active in achieving the results of the present invention, an alternative and more general expression of the amount of copolymer is one based on the amount of silicon in the total composition. Thus, the amount of the polycarbonate-siloxane copolymer in the compositions of the invention is appropriately expressed as an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition, for example 3.6% by weight.

The compositions of the invention also contain a colorant composition comprising titanium dioxide. The selection of the titanium dioxide component is important in the context of the present invention, because as illustrated in the Comparative Examples, some titanium dioxide materials lead to a significant reduction in the fire-retardancy of the composition. Without intending to be bound by any particular mechanism, it is believed that this degradation of properties arises as a result of different distribution of black pigment, for example carbon black and titanium dioxide formulations producing unsuitable results. Specifically, microscopic evaluation shows fairly even dispersion of black pigment particles, while undesirable types of titanium dioxide are seen to aggregate, apparently with the siloxane of the polycarbonate-siloxane copolymer. This problem is alleviated in the present invention by maintaining a minimum level of polycarbonate-siloxane copolymer which is dependent on the thickness of the material to be molded, and through the use of titanium dioxide having an organic coating, and optionally an additional inorganic coating. Commercially available TiO_2 pigments are typically prepared from colloidal suspensions in which low levels of alumina are added to chemically passivate the pigment surface. A secondary organic coating, for example an organo-silicone coating, is then applied to

further reduce surface reactivity and improve handling characteristics. While the exact coating formulations are often kept proprietary by the supplier, the general compositions of the organic coating and whether or not Al_2O_3 is used is frequently known. Specific examples of suitable titanium dioxide preparations that are commercially available include Tioxide R-FC5 (Huntsman), a small crystal product coated with TMP (trimethylolpropanol), PDMS (polydimethylsiloxane) and Al_2O_3 ; Titafrance RL91, a small crystal product coated with 1.2% PDMS silicone oil; and Kronos 2230, a normal-sized crystal product coated with PDMS polysiloxane and Al_2O_3 . Based on results using these materials, the claimed invention encompasses TiO_2 with an organic coating, and in particular an organic coating comprising a polysiloxane, TMP or mixtures thereof.

The amount of titanium dioxide is suitably from 1 to 2.0 % by weight of the total composition, preferably 1 to 1.5 weight percent. Higher amounts of the polycarbonate-siloxane copolymer facilitate the inclusion of higher amounts of titanium dioxide.

In addition to titanium dioxide, the colorant composition may include dyes, pigments or other colorants which in combination with the titanium dioxide produce an overall light coloration in the composition. The colorant composition may also comprise visual effects materials such as metallic-effect pigment, a metal oxide-coated metal pigment, a platelike graphite pigment, a platelike molybdenum disulfide pigment, a pearlescent mica pigment, a metal oxide-coated mica pigment, an organic effect pigment, a layered light interference pigment, a polymeric holographic pigment or a liquid crystal interference pigment. In one embodiment, the effect pigment is a metal effect pigment selected from the group consisting of aluminum, gold, brass and copper metal effect pigments; especially aluminum metal effect pigments. In another embodiment, the effect pigments are pearlescent mica pigments or a large particle size, preferably platelet type, organic effect pigment selected from the group consisting of copper phthalocyanine blue, copper phthalocyanine green, carbazole dioxazine, diketopyrrolopyrrole, iminoisoindoline, iminoisoindolinone, azo and quinacridone effect pigments.

The thermoplastic composition may optionally comprise a rubbery impact modifier. When present, the impact modifier copolymer resin is suitably added to the thermoplastic composition in an amount between about 1 and 30 % by weight and may comprise one of several different rubbery modifiers such as graft or core shell rubbers or combinations of two or more of these modifiers. Suitable are the groups of modifiers known as acrylic rubbers, ASA rubbers, diene rubbers, organosiloxane rubbers, EPDM rubbers, styrene-butadiene-styrene (SBS) or styrene-ethylene-butadiene-styrene (SEBS) rubbers, ABS rubbers, MBS rubbers and glycidyl ester impact modifiers.

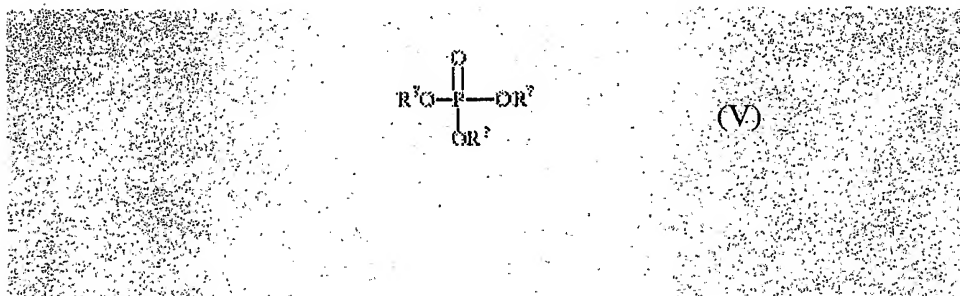
The composition may also include an anti-drip agent such as a fluoropolymer. The fluoropolymer may be a fibril forming or non-fibril forming fluoropolymer. Preferably the fluoropolymer is a fibril forming polymer. In some embodiments polytetrafluoroethylene is the preferred fluoropolymer. In some embodiments it is preferred to employ an encapsulated fluoropolymer i.e. a fluoropolymer encapsulated in a polymer as the anti-drip agent. An encapsulated fluoropolymer can be made by polymerizing the polymer in the presence of the fluoropolymer. Alternatively, the fluoropolymer can be pre-blended in some manner with a second polymer, such as for, example, an aromatic polycarbonate resin or a styrene-acrylonitrile resin as in, for example, U.S. Patent Nos. 5,521,230 and 4,579,906 to form an agglomerated material for use as an anti-drip agent. Either method can be used to produce an encapsulated fluoropolymer.

The fluoropolymer in the encapsulated fluoropolymer comprises a fluoropolymer with a melting point of greater than or equal to about 320°C, such as polytetrafluoroethylene. A preferred encapsulated fluoropolymer is a styrene-acrylonitrile copolymer encapsulated polytetrafluoroethylene (i.e., TSAN). TSAN can be made by copolymerizing styrene and acrylonitrile in the presence of an aqueous dispersion of polytetrafluoroethylene (PTFE). TSAN can, for example, comprise about 50 wt% PTFE and about 50 wt% styrene-acrylonitrile copolymer, based on the total weight of the encapsulated fluoropolymer. The styrene-acrylonitrile copolymer can, for example, be about 75 wt% styrene and about 25 wt% acrylonitrile based on the total weight of the copolymer. TSAN offers significant

advantages over polytetrafluoroethylene, namely TSAN is more readily dispersed in the composition.

When present, the anti-drip agent is present in an amount effective to reduce the potential for dripping, for example in an amount of from 0.1 to 1.4 % by weight, more commonly 0.5 to 1% by weight.

The compositions of the invention may also contain an effective flame-retarding amount of a flame retardant. The flame retardant may comprise a phosphate based flame retardant or a sulfonate salt flame retardant. When the composition comprises flammable components such as alkylaromatic copolymers it is preferable for the flame retardant to comprise an organic phosphate flame retardant. The organic phosphate flame retardant is preferably an aromatic phosphate compound of the formula (V):



where R^7 is the same or different and is alkyl, cycloalkyl, aryl, alkyl substituted aryl, halogen substituted aryl, aryl substituted alkyl, halogen, or a combination of any of the foregoing, provided at least one R^7 is aryl. Suitable phosphate flame retardants include those based upon resorcinol such as, for example, resorcinol tetraphenyl diphosphate, as well as those based upon bis-phenols such as, for example, bis-phenol A tetraphenyl diphosphate (BPADP). Phosphates containing substituted phenyl groups are also suitable.

The flame retardant materials may also be a sulfonate salt such as Rimar salt (potassium perfluorobutane sulfonate) and potassium diphenylsulfone sulfonate. See also the perfluoroalkane sulfonates described in US Patent No. 3,775,367, which is incorporated herein by reference.

The compositions of the invention may also include other optional components of the type commonly employed in polycarbonate compositions. Such components include without limitations antioxidants, UV stabilizers, mold release agents, fillers such as clay, wollastonite, or talc, reinforcing agents such as glass fibers, and antistats.

The invention also provides articles, for example molded or extruded articles that have flame retardant properties. In assessing flame-retardance of a polycarbonate article, it is relevant to consider the point of minimum wall thickness, since this the region of the article that is most flammable. In the claims of this application, the minimum wall thickness is referred to as a "first thickness" and the article is formed from a molding composition comprising (a) a bulk polycarbonate resin component; (b) a polycarbonate-siloxane copolymer; and (c) a colorant composition comprising titanium dioxide, wherein the titanium dioxide has an organic coating, and the amount of polycarbonate-siloxane copolymer is selected such that molding composition achieves a V0 UL fire rating at the first thickness. Thus, the desired amount of polycarbonate-siloxane copolymer depends on the minimum thickness of the article and the amount of titanium dioxide and the type of organic coating. Suitable amounts at different thicknesses may vary somewhat depending on other components in the molding composition, however the following values provide exemplary guidance.

Thickness (mm)	Titanium Dioxide (coating) %	% polycarbonate-siloxane copolymer (containing 20% siloxane by weight)
1.6	(TMP/PDMS) 1-1.5	>18
2.0	(TMP/PDMS) 1-1.5	>15
3.0	(TMP/PDMS) 1-1.5	>8

The compositions of the invention are suitably used in a method for forming a light colored, flame retardant polycarbonate articles. This method comprises the steps of forming a blend comprising: (a) a bulk polycarbonate resin component; (b) a polycarbonate-siloxane copolymer in an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and (c) a colorant composition comprising titanium dioxide, wherein the amount of titanium dioxide is from 1 to 2.0 % by weight of the total composition; and forming an article from the blend. The blend may be formed in a melt extruder or other common equipment, and the article is suitably formed using known techniques for molding, for example injection molding, or by extrusion.

The application will now be further described with reference to the following non-limiting examples:

Example 1: Four grades of TiO₂ were obtained from commercial suppliers. The grades and their characteristics are summarized in Table 1. Samples of white compositions were prepared as outlined in Table 2, and tested for fire retardancy and melt viscosity. The compositions contained the following additives where indicated: a mold release agent, pentaerythritol tetrastearate, commercially available as PETS G from Faci (>90 percent esterified); a phosphite stabilizer, tris(2,4-di-tert-butylphenylphosphite), commercially available as IRGAFOS 168 from Ciba; a hindered phenol stabilizer, octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate, commercially available as IRGANOX 1076 from Ciba; Flame retardant available under the tradename NcendX P-30 (bisphenol A bis(diphenylphosphate), or BPADP) commercially available from Albemarle and T-SAN, a drip retardant encapsulated poly(tetrafluorethylene), obtained from General Electric Plastics Europe,

comprising 50 weight percent polystyrene acrylonitrile and 50 weight percent poly(tetrafluorethylene).

To prepare the samples, polycarbonate pellets of bisphenol-A polycarbonate made by a melt process with a Melt Flow rate, MVR @300°C, 1.2kg, of 23.5-28.5, target 26.0g/cm³ were combined with pellets of bisphenol-A polycarbonate made by a melt process with a Melt Flow rate, MVR @300°C, 1.2kg, of 5.1-6.9, target 6.0 g/cm³ (introduced via a powder feeder) and compounded on a Werner & Pfleiderer co-rotating twin screw extruder (25 millimeter screw) and subsequently molded according to ISO294 on a ENGEL injection molding machine, using Axxicon ISO Manufactured (AIM) Mould system for producing the UL bars specimens. Compositions were tested according to UL 94 standards for Vertical burning test V-0 at 1.6 millimeters. p(FTP) is the probability of a first time pass in the UL94 test. The results are set forth in Table 3.

Table 1						
Sample No.	Product Name	Description (per supplier)	Organic Coating	Inorganic Coating	% TiO ₂	Supplier
1	Tioxide R-FC5	small crystal, coated	TMP. PDMS	Al ₂ O ₃	97.5	Huntsman
2	Titafrance RL9	small crystal, coated	PDMS (1.2 %) silicone oil	—		Millenium
3	Kronos 2230	normal crystal, specially treated	PDMS polysiloxane	Al ₂ O ₃	96.0	Kronos
4	Titafrance RL11A	small crystal, unbolted	--	--		Millenium

Table 2

	No colorant control	Black	1	2	3	4	5	6	7	8	9	10	11
Pellet Polycarbonate	71.41	71.23	70.41	69.41	68.41	70.41	69.41	68.41	70.41	69.41	68.41	70.41	69.41
Powder feeder Polycarbonate	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8	11.8
polycarbonate-siloxane copolymer	12	12	12	12	12	12	12	12	12	12	12	12	12
BPADP	2	2	2	2	2	2	2	2	2	2	2	2	2
poly-SAN	2	2	2	2	2	2	2	2	2	2	2	2	2
TSAN	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
PETS (mold release)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Irgaphos 168	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09	0.09
Black Pigment		0.18											
TiO ₂ sample 1			1	2	3								
TiO ₂ sample 2						1	2	3					
TiO ₂ sample 3									1	2	3		
TiO ₂ sample 4												1	2

Table 3					
Formulation	FOT2 (sec)	Stdev- FOT2	p(FTP) V0 @ 1.6 mm	p(FTP) V1 @ 1.6 mm	MV@280°C, 1500 sec ⁻¹
No colorant control	3.4	1.8	0.91	0.99	216
Black pigment	2.6	1.8	0.92	1.00	210
1	4.8	4.3	0.52	0.98	212
2	5.4	2.2	0.72	1.00	214
3	7.5	2.9	0.15	1.00	212
4	12.5	4.8	0.00	0.89	207
5	11.0	4.3	0.00	0.98	211
6	13.6	8.5	0.00	0.85	214
7	6.9	2.6	0.29	1.00	209
8	8.4	5.8	0.04	0.96	207
9	9.6	4.4	0.01	0.99	211
10	8.9	3.4	0.02	0.99	
11	17.6	18.0	0.00	0.56	

As is apparent from the results, while the compositions with no colorant (NC) or black pigment (BK) had p(FTP) V0 @1.6 mm of greater than 0.9 (indicating a greater than 90% likelihood of passing this test), none of the TiO₂ containing formulations had a reasonable likelihood of passing. The melt viscosities were similar for each of the materials tested.

This example illustrates the unanticipated problem with using TiO₂ to make white or light colored products in such compositions.

Example 2: Formulations were prepared in which the amount of polycarbonate-siloxane copolymer was varied from 12% to 20% using Tioxide R-FC5™ (TiO₂ sample1) as indicated in Table 4.

Table 4												
	13	14	15	16	17	18	19	20	21	NC 2	BK2	BK3
Pellet Polycarbonate	70.49	70.3 4	69.8 4	69.3 4	69.3 4	68.3 4	67.8 4	66.3 4	65.8 4	70.8 4	71.1 6	71.1 6
Powder feeder Polycarbonate	11.95	11.8	11.3	10.8	9.8	9.8	9.3	7.8	7.3	12.3	11.8	11.8
polycarbonate-siloxane copolymer	12	12	12	14	14	16	16	20	20	12	12	12
BPADP	2	2	2	2	2	2	2	2	2	2	2	2
poly-SAN	2	2	2	2	2	2	2	2	2	2	2	2
TSAN	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
PETS (mold release)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Irgaphos 168	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
AO 1076	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08	0.08
Black Pigment											0.18	0.18
TiO ₂ sample 1	0.7	1	2	1	2	1	2	1	2			

The fire retardancy was tested for these samples and for 12% samples with no colorant (natural) or with black colorant. As reflected in Table 5, p(FTP) @ 1.6 mm of greater than 0.9 was achieved only in those TiO₂-containing sample having 1% TiO₂ or greater in which the level of Lexan-ST (a polycarbonate/polydimethylsiloxane (PC/PDMS) copolymer having 20% weight percent siloxane content based on the total weight of the copolymer and a block length of 50 units of the poly(diorganosiloxane)) was 20%. Fig. 1 shows the relationship between p(FTP)

and the % TiO₂ in these runs. As is apparent, increasing TiO₂ decreases the p(FTP) value.

Table 5					
Formulation	% TiO ₂	% PC-siloxane	FOT2 (sec)	Stdev (sec)	p(FTP) @ 1.6 mm
13	0.7	12	2.0	1.9	0.948
14	1	12	6.3	3.8	0.406
15	2	12	9.1	5.7	0.024
16	1	14	4.6	2.7	0.667
17	2	14	7.0	5.0	0.117
18	1	16	3.9	2.1	0.675
19	2	16	5.6	4.0	0.559
20	1	20	2.5	1.8	0.962
21	2	20	2.3	3.1	0.654
NC2	natural	12	3.6	1.2	0.919
BK1	black	12	2.3	1.5	0.992
BK2	black	12	1.7	1.6	0.986

Example 3: Theoretical modeling with %polycarbonate-siloxane levels =14.5-21% (PC/ST ratio=5.5 -3.5) indicated an optimum in the Design space of around 18% polycarbonate-siloxane content in compositions with a p(FTP) greater than or equal to 0.9. Samples were therefore prepared containing 18% polycarbonate-siloxane copolymer as indicated in Table 6 using the methods as set forth in Example 1. In addition to the components listed in Table 6, these compositions contained colorant components in total amounts less than 0.01 % by weight. Colorants used in combinations to achieve different colored products included MONARCH 800, BAYFERROX 180MPL, VERDE HELIOGEN K8730, AMARILLO SICOTAN K2001 FG, VERDE OXIDO DE CROMO, Pigment Yellow 119, AZUL SICOPAL

K6310 and ultramarine blue. The results of fire-retardance testing of these samples are set forth in Table 7.

Table 6						
	22	23	24	25	26	27
Pellet Polycarbonate	69.74	69.24	69.09	68.99	69.14	37.30
Powder feeder Polycarbonate	8	7.5	7.35	7.25	7.4	39.80
polycarbonate-siloxane copolymer	18	18	18	18	18	17.8
BPADP	2	2	2	2	2	2
poly-SAN	1	1	1	1	1	1
TSAN	0.8	0.8	0.8	0.8	0.8	0.4
PETS (mold release)	0.3	0.3	0.3	0.3	0.3	0.3
Irgaphos 168	0.08	0.08	0.08	0.08	0.08	0.08
TiO ₂ sample 1		1		1.5	1.2	1.3
TiO ₂ sample 2			1.3			

Table 7					
Formulation	% TiO ₂	% PC-siloxane	FOT2 (sec)	Stdev	p(FTP) @ 1.6 mm
22	0	18	3.1	2.9	0.987
23	1	18	3.7	2.1	0.856
24	1.3	18	4.1	1.9	0.880
25	1.5	18	2.7	2.0	0.937
26	1.2	18	4.7	1.8	0.887
27	1.3	17.8	4.4	1.7	0.987

Claims

1. A composition comprising:
 - (a) a bulk resin component comprising a polycarbonate resin;
 - (b) a polycarbonate-siloxane copolymer with a siloxane content and in an amount sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and
 - (c) a colorant composition comprising titanium dioxide having an organic coating, preferably comprising an organosiloxane or trimethylolpropanol, wherein the amount of titanium dioxide is from 1 to 2.5 % by weight of the total composition.
2. The composition of claim 1 having one or more of the following characteristics:
 - (a) the bulk resin component makes up at least 50% of the composition;
 - (b) the bulk resin component further comprises an engineering thermoplastic, preferably a styrene acrylonitrile copolymer or polymethyl(methacrylate);
 - (c) the colorant composition comprises from 1 to 1.5% by weight of the total composition;
 - (d) the organic coating comprises an organosiloxane or trimethylolpropanol; or
 - (e) the amount of titanium dioxide is from 1 to 1.5% by weight of the total composition.
3. The composition of any of the preceding claims further comprising one or more of the following:
 - (a) a rubbery impact modifier;
 - (b) an antidrip agent; or
 - (c) a flame retardant not being a polycarbonate-siloxane copolymer.

4. The composition of claim 3 having one or more of the following characteristics:

(a) the rubbery impact modifier is selected from the group consisting of acrylic rubbers, ASA rubbers, diene rubbers, organosiloxane rubbers, EPDM rubbers, styrene-butadiene-styrene (SBS) or styrene-ethylene-butadiene-styrene (SEBS) rubbers, ABS rubbers, MBS rubbers and glycidyl ester impact modifiers, and mixtures thereof;

(b) the rubbery impact modifier is present in an amount of from 1 to 30% by weight;

(c) the antidrip agent is styrene-acrylonitrile copolymer encapsulated polytetrafluoroethylene; or

(d) the flame retardant is a phosphate flame retardant, preferably bis-phenol A tetraphenyl diphosphate, or a sulfonate, preferably a perfluoroalkane sulfonate, such as potassium perfluorobutane sulfonate.

5. An article, made of the composition of claims 1-4 having one or more wall thicknesses greater than or equal to a first thickness, said article being formed from a molding composition according to claims 1-4 the amount of polycarbonate-siloxane copolymer is selected such that molding composition achieves a V0 UL fire rating at the first thickness.

6. The article of claim 5 having a first thickness of 1.6 mm.

7. A method for forming a light colored, flame retardant polycarbonate article comprising the steps of forming a blend as defined in claims 1-4; and

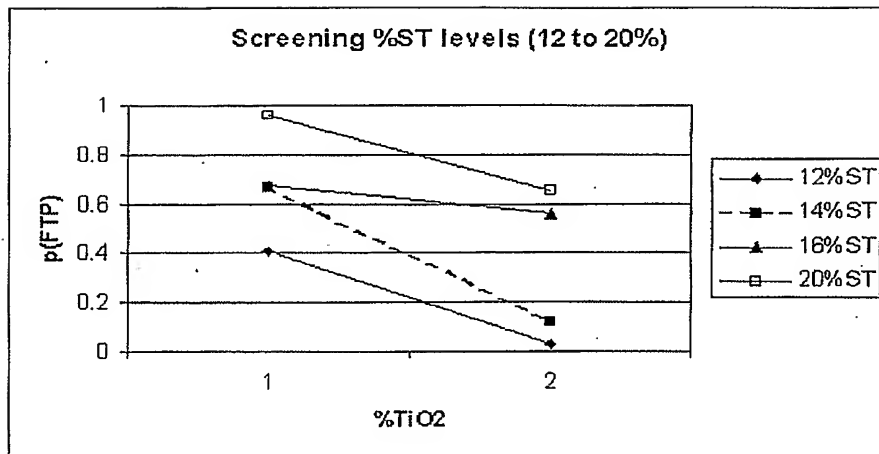
forming an article from the blend.

8. A method for enhancing the flame retardance of a light colored composition comprising a bulk resin component comprising polycarbonate; a polycarbonate-

siloxane copolymer; and a colorant composition comprising titanium dioxide, said method comprising the steps of

- (a) using the polycarbonate-siloxane copolymer in a quantity sufficient to provide an amount of siloxane of at least 3% by weight of the total composition; and
- (b) selecting as the titanium dioxide a titanium dioxide having an organic coating comprising a polyorganosiloxane, trimethylolpropanol, or mixtures thereof.

1/1

**Fig. 1**

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/033673

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L69/00 C08K9/04 C08K3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 524 731 A (GEN ELECTRIC) 27 January 1993 (1993-01-27) Inventions 5,7-9,11 page 2, line 17 - line 22	1-8
Y	page 4, line 55 - line 58; tables	1-8
Y	US 6 133 360 A (CHEN FRED FUH-SHENG ET AL) 17 October 2000 (2000-10-17) column 12, line 23 - line 31; claims; table I column 13, line 21 - line 25	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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